

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION.

### Improvements in and relating to Metal Plating.

We, UNION CARBIDE CORPORATION, of 270 Park Avenue, New York, State of New York, United States of America, a corporation organised under the laws of the State of New York, United States of America, (Assignee of ROY LAVELLE PRUETT and WILLIAM ROBERT MYERS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to metal plating processes, and is especially concerned with a process for depositing a metal plate on a solid substrate from a readily decomposable transition metal-bearing compound.

The plating of a solid substrate with a transition metal is, in general, known to the art, and has been found to provide a variety of useful articles. By way of illustration, the metallic coatings and films thus produced exhibit useful and desirable electrical conductance properties, furnish corrosion resistance and result in striking, mirror-like decorative effects.

Heretofore, the plating of a solid substrate with a transition metal such as chromium, for example, has often been carried out by conventional electroplating techniques. However, such processes have not met with complete satisfaction since they generally require the utilization of complex plating equipment, as well as extended periods of operation, to produce commercially acceptable plates, i.e., plates having a thickness of about  $2 \times 10^{-4}$  inch, or more. It is also difficult to obtain uniform plates on irregularly shaped objects by means of electroplating techniques due to the increased electrical density engendered at pointed or highly curved surface areas of the substrate. In addition, electroplating

techniques are inherently limited to use in connection with electrically conductive substrates such as metals. Hence, their use in plating glass, wood, ceramics or other solid, electrically non-conductive materials is precluded. Moreover, the electroplating of solid substrates with transition metals other than chromium, such as vanadium or molybdenum, for instance, has frequently been found unamenable to large scale operations.

Alternatively, transition metals can be deposited on solid substrates by means of conventional gas plating techniques. However, these latter plating processes also generally necessitate the use of complex equipment, as well as extended periods of operation, i.e. plating periods of about 30 minutes or more, to produce commercially acceptable plates. In addition, gas plating techniques are usually limited in that the thickness of the plate produced thereby ordinarily cannot readily be varied so as to meet the requirements of diverse applications for the plate.

It has been found that the disadvantages hereinabove described can now be overcome to a significant extent through the practice of the present invention, an object of which is to provide a convenient process for the rapid deposition of transition metals on a solid substrate in the form of an adherent plate having a controllable thickness of about  $2 \times 10^{-4}$  inch, or more. Another object of this invention is to provide a process for the deposition of a transition metal on a solid substrate in the form of a substantially pure, uniformly thick plate. A further object of this invention is to provide for the deposition of a transition metal on a solid substrate by a process which is capable of reproducing plates with a high degree of consistency insofar as plate thickness is concerned. Still other objects will become

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apparent from the description which follows below:—

In its broadest aspect, the process of this invention contemplates the plating of a solid substrate by uniformly contacting the surface of the substrate over the area to be plated with a plating solution containing a readily decomposable bis(arene) transition metal compound in an inert liquid organic solvent having a boiling point above 200° C., and preferably, in a high-molecular weight liquid alkane. Such contact is necessarily effected while the substrate is at an elevated temperature which is above the decomposition temperature of the bis(arene) transition metal compound, and entails the use of a plating solution which is at a temperature of from 20° C. to 100° C. The period of contact can vary broadly and need only be sufficient to provide for the deposition of a plate of commercially acceptable thickness, such period being readily determinable by one skilled in the art in light of this disclosure. It is also preferred that the process of this invention be carried out in an inert atmosphere, i.e., in the absence of oxygen or oxygen-containing substances which can react with the bis(arene) transition metal compound or with the resulting metal plate itself, to form metal oxides which may contaminate the metal plate.

The bis(arene) transition metal compounds which are useful in the plating process of this invention are organo-metallic compounds in which the arene groups are uncharged aromatic hydrocarbons containing either an isolated benzene ring or an aryl-substituted benzene structure. As employed in this application, the term "isolated benzene ring" is meant to define a benzene ring as contained in benzene itself or in a fused ring polycyclic aromatic hydrocarbon containing a benzene ring wherein, by the Kekule formulation, any double bond in a ring fused to such benzene ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms. The term "isolated benzene ring" is also meant to define a benzene ring as contained in a monocyclic aromatic hydrocarbon having one or more aliphatic substituents on a benzene ring wherein any double bond external to the benzene carbon ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms. Thus, benzene, indane, tetrahydronaphthalene, 9,10-dihydroanthracene, 9,10-dihydronaphthalene, alkyl-substituted benzenes, such as toluene, ethylbenzene, butylbenzene, octylbenzene, etc., and alkenyl-substituted benzenes in which double bonds external to the benzene ring are separated therefrom by at least two carbon atoms, such as allylbenzene, and the like, are examples of aromatic hydrocarbons containing an isolated benzene ring.

By contrast naphthalene, indene, anthracene, phenanthrene and styrene are examples of aromatic hydrocarbons which do not contain an isolated benzene ring.

As also mentioned above, a class of aromatic hydrocarbons which do not contain an isolated benzene ring, namely aryl-substituted benzenes, also form bis(arene) transition metal compounds which are useful in the plating process of this invention. Examples of such aryl-substituted benzenes are polyphenyls, alkyl-substituted polyphenyls such as *p*-isopropylidiphenyl and *p*-*p'*-dimethyldiphenyl, phenylanthracene and phenylphenanthrene.

The bis(arene) transition metal compounds contemplated by this invention may, from the point of view of their organic moiety, be characterized as addition compounds in contrast to organo-metallic substitution compounds wherein hydrogen or another substituent of the organic nucleus is substituted or removed in forming the organo-metallic compound. Thus, the bis(arene) transition metal compounds used in the process of this invention are to be distinguished from the organo-metallic compounds formed by the chemical bonding of a cyclopentadienyl radical with an element (Fischer and Pfab, *Zeit. für Naturforschung*, 7b, page 377, (1952)), and from phenyl mercury compounds, e.g., phenyl mercuric acetate (U.S. Patent 2,502,222). Formation of such substitution compounds, it is to be noted, involves elimination of hydrogen from the cyclopentadiene or benzene nucleus. In the case of the bis(arene) transition metal compounds of the present invention, the chemical union of the transition element with the aromatic hydrocarbon does not involve the elimination of hydrogen or any other substituent of the organic nucleus. The bis(arene) transition metal compounds may, therefore, be regarded as the addition products of transition elements with aromatic hydrocarbons.

The bis(arene) transition metal compounds contemplated by this invention can be represented more clearly by the formula:—



wherein Ar designates either an aromatic hydrocarbon containing an isolated benzene ring, or an aryl-substituted benzene, as hereinabove described, and M designates a transition metal of groups VA and VIA of the Periodic Table as defined in Webster's New Collegiate Dictionary, 1956, p. 626, and those having an atomic number of from 23 to 74, vanadium, chromium, niobium, molybdenum, tantalum and tungsten. The bis(arene) transition metal compounds can also have mixed Ar substituents, as more specifically represented by the formula:—



wherein Ar and Ar' independently designate members of the same class of aromatic hydrocarbons and M designates a transition metal as hereinabove defined. The exact nature of the bond between the aromatic hydrocarbon moiety and the transition metal is unknown. However, it is known that the isolated benzene ring or the benzene ring of the aryl-substituted benzene is complexed to the transition metal.

The bis(arene) transition metal compounds contemplated by this invention include, by way of illustration, bis(benzene)chromium, bis(benzene)molybdenum, bis(tetrahydronaphthalene)chromium, bis(benzene)vanadium, bis(toluene)chromium, bis(toluene)vanadium, bis(toluene)molybdenum, bis(mesitylene)chromium, bis(hexamethylbenzene)chromium, bis(ortho-xylene)chromium, bis(meta-xylene)chromium, bis(para-xylene)chromium, bis(octylbenzene)chromium, bis(mesitylene)molybdenum, bis(benzene)tungsten, bis(toluene)tungsten, bis(benzene)chromium, bis(tetrahydronaphthalene)chromium, bis(diphenyl)chromium, bis(benzene)niobium, bis(benzene)tantalum, bis(diphenyl)molybdenum, bis(cumene)molybdenum and bis(cumene)chromium. The preferred bis(arene) transition metal compounds are those in which the arene moiety is either benzene or a lower alkyl-substituted benzene in which the lower alkyl substituent(s) contain from 1 to 8 carbon atoms and more preferably from 1 to 4 carbon atoms.

Moreover, as herein described, the process of this invention is directed particularly to the use of the bis(arene) transition metal compounds in which the transition metal is a group Va or group VIA element of the Periodic Table. Such metals form the neutral or uncharged bis(arene) metal compounds contemplated by this invention, as opposed to other transition metals which form only salt-like compounds containing an arene metal cation, e.g., dimesitylene iron dibromide.

The bis(arene) transition metal compounds can be prepared by reacting an anhydrous transition metal salt, preferably a transition metal halide, with an aromatic hydrocarbon containing at least one isolated benzene ring, or with an aryl-substituted benzene, in the presence of an anhydrous aluminum halide and a reducing agent.

In an embodiment of the present invention, a heated, solid substrate is uniformly contacted over the surface to be plated with a high-molecular weight alkane solution of the bis(arene) transition metal compound. Such contact can be effected, for example, by dipping a heated substrate into the plating solution. A technique of this nature is commonly referred to as dip plating.

During the plating operation, the temperature of the substrate must be above the de-

composition temperature of the bis(arene) transition metal compound to effect the deposition of a metal plate, such temperature being readily ascertainable by one skilled in the art in light of this disclosure. In general, the decomposition temperature of the bis(arene) transition metal compound will vary, for instance, in the range of from 200° C. in the case of bis(arene)molybdenum compounds to 350° C. to 400° C. in the case of bis(arene)chromium and bis(arene)vanadium compounds. Moreover, the substrate is preferably heated to a temperature of 150° C. to 400° C. above the decomposition temperature of the bis(arene) transition metal compound, with thicker plating ordinarily being obtained as the temperature of the substrate is increased. At substrate temperatures above 700° C. to 800° C., deposition of the transition metal also occurs. However, when the substrate is at such elevated temperatures, the aromatic hydrocarbon moiety of the bis(arene) transition metal compound with which the substrate is contacted tends to decompose rapidly giving off carbon and/or polymerizable hydrocarbons such as ethylene and acetylene, which may contaminate the resulting metal plate. Hence, the upper operable temperature to which the substrate can be heated in accordance with the process of this invention is, for practical purposes, determined by the decomposition (cracking) temperature of the aromatic hydrocarbon moiety of the bis(arene) transition metal compound. In addition, this temperature is also dependent to a certain extent upon the nature and size of material chosen as the substrate. Thus, for example, somewhat higher preheat temperatures of 650° C., and higher, are best employed in connection with the dip plating of non-conducting materials such as glass or porcelain with chromium, as compared with the dip plating of metal substrates, which are best preheated to a temperature of up to 500° C., under otherwise similar operating conditions. Furthermore, thinner substrate specimens must ordinarily be preheated to somewhat higher temperatures than thicker ones in connection with dip plating operations due to their difference in heat capacity.

The use of a high-molecular weight, relatively non-volatile alkane solvent for the bis(arene) transition metal compound in forming the plating solution of this invention is, as hereinabove described, preferred. The use of such a solvent, it is believed, is responsible, at least in part, for the fact that thicker plates advantageously can be produced by the process of this invention within substantially shorter periods of operation than are obtained by means of prior art plating processes. In this connection, it has been found, for example, that the alkane

employed as the solvent must be a compound containing at least 12 carbon atoms, and preferably contains from 16 to 22 carbon atoms. Suitable alkane solvents include, for example, dodecane, tetradecane, hexadecane, methylpentadecane, heptadecane, ethylpentadecane, isopropyltetradecane, octadecane, isopropylpentadecane, docosane, and pentatriacontane. When using alkane solvents containing less than 12 carbon atoms, i.e., having a boiling point below 200° C., metal plates having a commercially acceptable thickness are either not obtained or require an inordinately long period of operation for their production. On the other hand, the upper limit for the molecular weight of the alkane solvent is determined by the necessity for having a liquid plating solution present during the practice of this invention. Hence, the alkane solvent should have a melting point no higher than 100° C.

Also of importance to the plating process of this invention as herein described is the temperature of the plating solution. The temperature of the solution, it can be seen, is necessarily above the melting point of the solvent to assure the presence of a liquid plating solution, and can vary in the range of from 20° C. to 100° C. during the plating operation. A solution temperature of from 25° C. to 90° C. is preferred. When the heated substrate is dipped into a plating solution which is at a temperature substantially above 100° C., an undesirable blackening or darkening of the resulting metal plate is ordinarily encountered. On the other hand, a solution temperature substantially below 20° C. is ordinarily avoided so as to preclude an excessively rapid quenching of the heated substrate. It is to be noted that since the substrate is necessarily heated to above the decomposition temperature of the bis(arene) transition metal compound, such temperature being above 100° C., control consistent with the maintenance of a temperature of from 20° C. to 100° C. for substantially all of the plating solution is desirably exerted during the plating process. Such control can be effected, for example, by externally cooling the plating solution, by stirring the solution, by limiting the period of contact between the plating solution and the heated substrate, or in any other convenient manner.

The concentration of the bis(arene) transition metal compound which is dissolved in the high-molecular weight alkane solvent to produce the plating solution of this invention can vary in the range of from 5 per cent up to 60 per cent by weight based upon the weight of the solution, with best results being obtained using a plating solution containing from 20 per cent to 50 per cent by weight of the bis(arene) transition metal compound. As the concentration of the bis(arene) transi-

tion metal compound in the plating solution is increased beyond the broad range indicated above, the resulting metal plates ultimately obtained therefrom by the process of this invention tend to evidence an increasing number of dark streaks believed to be carbon deposits. It has also been found that, within the aforementioned concentration range, the thickness of the resulting metal plate varies directly with the initial concentration of the bis(arene) transition metal compound. Thus, advantageously, by controlling the concentration of the bis(arene) transition metal compound in the plating solution under otherwise constant reaction conditions, metal plates of controlled thickness can be obtained.

Another advantage that accrues from the practice of this invention as herein described resides in the short periods of operation required to deposit a metal plate of commercially acceptable thickness. Commercially acceptable plates can be obtained, for example, by dipping the heated substrate in the plating solution for a contact period of 5 to 15 seconds, although longer contact periods can also be employed. To reproduce a plate of the same quality and thickness using conventional plating processes, such as gas plating techniques, may require a period of operation of the order of 30 minutes or more. Thus, because of the shorter plating periods which can be employed, the process of this invention is readily adaptable to continuous operation. In addition, the metal plated substrates produced in accordance with this invention can be replated in similar manner, if desired, to obtain thicker plates without a detectable loss of the physical properties of the original plate. Other methods for obtaining thicker plates in accordance with the process of this invention lie in an extension of the plating period, an increase in the concentration of the bis(arene) transition metal compound in the plating solution, the selection of a particular solvent for the plating solution and/or an increase in temperature of the substrate, with which the plating solution is contacted, under otherwise constant reaction conditions.

Any platable solid substrate which is thermally stable at the temperature encountered can be used in the plating process of this invention in a variety of shapes or forms. By way of illustration, suitable substrates include glass, ceramics, metals such as copper, aluminum, iron, stainless steel and silver.

The invention can be illustrated further by description in connection with the following examples of its practice.

#### EXAMPLE I.

In a series of experiments, a chromium

plate was deposited on five  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch mild steel specimens by heating the steel specimens to elevated temperatures as indicated below in Table I and dipping the heated steel specimens under an atmosphere of nitrogen into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in *n*-octadecane. The plating solution was maintained at a temperature of 35° C. during the plating operation by means of a surrounding bath. After a contact period of 1 minute, each of the even, chromium-plated steel specimens thus formed were removed from the plating solution, washed with soap and water, dried with acetone and subsequently tested for plate continuity by exposing the specimens to the corrosive atmosphere of air at 100 per cent humidity for 3 hours. The corrosion test indicated the resulting chromium-plated steel specimens to be uniformly and effectively resistant to corrosion.

The thicknesses of the chromium plates obtained at the various heating temperatures are tabulated below in Table I wherein the heating temperature is the temperature to which the steel specimen was heated prior to contact with the plating solution.

TABLE I.

Heating Temperature (°C.)	Plate Thickness ( $\times 10^{-6}$ inch)
300	3.7
325	7.1
350	12.3
600	22.3
650	30.8

A 0.5 inch  $\times$  2 inches  $\times$  0.009 inch specimen of can stock steel was heated to a temperature of 650° C. and contacted with a 50 per cent by weight solution of bis(cumene)chromium in *n*-octadecane in a manner similar to that described above in

this example. The thickness of the resulting chromium plate having thus deposited on the steel specimen was found to be  $5.2 \times 10^{-6}$  inch.

## EXAMPLE II.

In a manner similar to that described in Example I, a  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch mild steel specimen was heated to a temperature of 600° C. and, under a nitrogen atmosphere, dipped into 60 milliliters of a 50 per cent by weight solution of bis(cumene)chromium in dodecane, the solution being maintained at a temperature of 35° C. After a contact period of 1 minute, the steel specimen was removed from the solution, washed and dried. The specimen was found to have an even chromium plate of  $7 \times 10^{-6}$  inch deposited thereon. However, when decane and heptane were independently substituted for dodecane under otherwise identical operating conditions to that described above in this example, no definable plate was obtained.

## EXAMPLE III.

A specimen of can stock steel, 0.5 inch  $\times$  2 inches  $\times$  0.009 inch, was heated to a temperature of 650° C. and, under a nitrogen atmosphere, dipped in a plating solution containing 50 per cent by weight of bis(cumene)chromium in *n*-octadecane. During the plating operation, the temperature of the plating solution was maintained at 35° C. by means of a surrounding bath. After a contact period of 15 seconds, the steel specimen was removed from the plating solution, washed with soap and dried with acetone. The thickness of the resulting chromium plate which had deposited on the specimen was then determined. Thereafter the process was repeated, yielding a plate of increasing thickness, until the plate began to show signs of cracking or spalling. The increase in plate thickness with each dip is indicated below in Table II, together with the total thickness of the plate at the conclusion of each dip.

TABLE II.

Dip Number	Increase in Plate Thickness ( $\times 10^{-6}$ inch)	Total Plate Thickness ( $\times 10^{-6}$ inch)
95	1	5.6
	2	9.5
	3	13.4
	4	17.7
	5	21.6
	6	25.5
100	7	29.8
	8	33.2
	9	36.6
	10	40.5
105	11	43.9
	12	47.3

TABLE II—cont.

	Dip Number	Increase in Plate Thickness ( $\times 10^{-6}$ inch)	Total Plate Thickness ( $\times 10^{-6}$ inch)
5	13	3.9	51.2
	14	3.9	55.1
	15	3.4	58.5
	16	3.0	61.5
	17	3.4	64.9
10	18	3.9	68.8
	19	3.0	71.8

## EXAMPLE IV.

In a manner similar to that described in Example III, a  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch mild steel specimen was heated to a temperature of 600° C. and, under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in *n*-octadecane and maintained at a temperature of 35° C., for a contact period of 1 minute. The steel specimen was then removed from

the plating solution, washed and dried, whereupon the thickness of the resulting chromium plate which had deposited on the specimen was determined. The process was repeated yielding a plate of increasing thickness. Some spalling of the plate was observed after the 16th dip. The spalling then became more evident after each successive dip. The test results obtained from this series of experiments are tabulated below in Table III.

TABLE III.

	Dip Number	Increase in Plate Thickness ( $\times 10^{-6}$ inch)	Total Plate Thickness ( $\times 10^{-6}$ inch)
35	1		23.0
	2	19.7	42.7
	3	21.6	64.3
	4	24.2	88.5
40	5	20.8	109.3
	6	22.7	132.0
	7	21.6	153.6
	8	21.9	175.5
45	9	21.2	196.7
	10	21.9	218.6
	11	21.6	240.2
	12	21.9	262.1
50	13	21.0	283.1
	14	22.7	305.8
	15	21.9	327.7
	16	21.0	348.7
55	17	20.2	368.9
	18	20.2	389.1
	19	21.3	410.4
	20	20.2	430.6
	21	18.2	448.8

## EXAMPLE V.

In a series of experiments conducted in a manner similar to that described in Example I, two  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch mild steel specimens were heated to a temperature of 550° C. and 600° C., respectively, and under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 50 per cent by weight of

bis(cumene)chromium in a refined kerosene having a distillation range of from 394° F. to 510° F. and consisting mainly of alkanes having at least 12 carbon atoms and a melting point up to 100° C. The plating solution was maintained at a temperature of 35° C. during the plating operation. After a contact period of about 15 seconds, the chromium plated steel specimens thus

formed were removed from the plating solution. The chromium plate having deposited on the steel specimen which was initially heated to a temperature of 550° C. was found to be  $5.9 \times 10^{-6}$  inch thick; while the chromium plate having deposited on the steel specimen which was initially heated to a temperature of 600° C. was found to be  $11.9 \times 10^{-6}$  inch thick.

A 0.5 inch  $\times$  2 inches  $\times$  0.009 inch specimen of can stock steel was heated to a temperature of 650° C. and contacted with a 50 per cent by weight solution of bis(cumene)chromium in *n*-octadecane in a manner similar to that described above in this example. The thickness of the resulting chromium plate having deposited on the steel specimen was found to be  $3.4 \times 10^{-6}$  inch.

#### EXAMPLE VI.

In a series of experiments conducted in a manner similar to that described in Example I, two  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch brass specimens were heated to a temperature of 500° C. and 550° C., respectively, and, under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 20 per cent by weight of bis(toluene)molybdenum in *n*-octadecane. The plating solution was maintained at a temperature of 35° C. during the plating operation. After a contact period of 15 seconds, the brass specimens were removed from the plating solution and found to have even, bright molybdenum plates of commercially acceptable thickness deposited thereon.

#### EXAMPLE VII.

In a series of experiments conducted in a manner similar to that described in Example I, three  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch brass specimens were heated to elevated temperatures of 550° C., 600° C. and 650° C., respectively, and, under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 20 per cent by weight of bis(toluene)vanadium in *n*-octadecane. The plating solution was maintained at a temperature of 35° C. during the plating operation. After a contact period of 15 seconds, the brass specimens were removed from the plating solution and found to have even vanadium plates of commercially acceptable thickness deposited thereon.

#### EXAMPLE VIII.

A porcelain combustion boat was cleaned with chromic acid and heated in an argon atmosphere to a temperature of 650° C. The heated porcelain boat was then dipped, under a nitrogen atmosphere, into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in *n*-octadecane. The plating solution was maintained at a temperature of 35° C. during the plating

operation. After a contact period of 2 minutes, the porcelain boat was removed from the plating solution and found to have an even, electrically conductive chromium plate of commercially acceptable thickness deposited thereon.

#### EXAMPLE IX.

A  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch flat Pyrex (a Registered Trade Mark) glass specimen was cleaned with chromic acid and heated in an argon atmosphere to a temperature of 650° C. The heated glass specimen was then dipped, under a nitrogen atmosphere, into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in *n*-octadecane. The plating solution was maintained at a temperature of 95° C. during the plating operation. After a contact period of 30 seconds, the glass specimen was removed from the plating solution and found to have an even, reflective chromium plate of commercially acceptable thickness deposited thereon. In similar manner, glass fibers are also plated with chromium by the process of this invention.

#### EXAMPLE X.

In a manner similar to that described in Example I, a  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch brass specimen was heated to a temperature of 550° C. and, under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in a refined mineral oil having a distillation range of from 656° F. to 934° F. and consisting mainly of alkanes having at least 12 carbon atoms and a melting point up to 100° C. The plating solution was maintained at about room temperature during the plating operation. After a contact period of 15 seconds, the brass specimen was removed from the plating solution and found to have an even chromium plate of commercially acceptable thickness deposited thereon.

#### EXAMPLE XI.

In a manner similar to that described in Example I, a  $\frac{1}{2}$  inch  $\times$  2 inches  $\times$   $\frac{1}{16}$  inch mild steel specimen was heated to a temperature of 550° C. and, under a nitrogen atmosphere, dipped into 60 milliliters of a plating solution containing 50 per cent by weight of bis(cumene)chromium in a refined mineral oil having distillation range of from 656° F. to 934° F. and consisting mainly of alkanes having at least 12 carbon atoms and a melting point up to 100° C. The plating solution was maintained at room temperature during the plating operation. After a contact period of 15 seconds, the steel specimen was removed from the plating solution and found to have an even

chromium plate  $14 \times 10^{-6}$  inch thick deposited thereon.

# WHAT WE CLAIM IS:—

1. A process for depositing a metal plate on a solid substrate which comprises the steps of heating said substrate, dipping the heated substrate into a liquid plating solution having a temperature maintained in the range of from  $20^{\circ}$  C. to  $100^{\circ}$  C. and comprising an alkane containing at least 12 carbon atoms, having a melting point up to  $100^{\circ}$  C., and having dissolved therein from 5 per cent to 60 per cent by weight based upon the weight of said plating solution of a bis(arene) transition metal compound of the general formula:—



wherein Ar designates an aromatic hydrocarbon containing an isolated benzene ring or an aryl-substituted benzene, and M designates a group VA or VIA metal of the Period Table having an atomic number of from 23 to 74, said substrate being brought into contact with said plating solution while said substrate is at a temperature above the decomposition temperature of said bis(arene) transition metal compound, and maintaining said substrate in contact with said plating solution for a period of time sufficient to deposit a metal plate on said substrate.

2. The process according to Claim 1 wherein the liquid solution is maintained at a temperature of from  $25^{\circ}$  C. to  $90^{\circ}$  C.
3. The process according to Claim 1 or 2 wherein the substrate is heated to a temperature of from  $150^{\circ}$  C. to  $400^{\circ}$  C. above the temperature of decomposition of the bis(arene) transition metal compound.
4. The process according to any of the

preceding claims wherein the concentration of the bis(arene) transition metal compound in the plating solution is from 20 to 50 per cent by weight based upon the weight of said solution.

5. The process as claimed in any of the preceding claims in which the transition metal is vanadium, chromium, niobium, molybdenum, tantalum or tungsten.

6. The process as claimed in any of the preceding claims in which the arene is benzene or an alkyl substituted benzene having from 1 to 8 carbon atoms in the alkyl group(s).

7. The process as claimed in Claim 6 in which the alkyl group(s) contains 1 to 4 carbon atoms.

8. The process according to any of the preceding claims wherein the bis(arene) transition metal compound is bis(cumene) chromium, bis(toluene) molybdenum, or bis(toluene) vanadium.

9. The process as claimed in any of the preceding claims in which the alkene contains 16 to 22 carbon atoms.

10. The process according to any of the preceding claims wherein the alkane is octadecane.

11. The process as claimed in any of the preceding claims which is effected in an inert atmosphere.

12. A process for depositing a metal plate on a solid substrate as hereinbefore described with reference to and as illustrated in any of the examples.

13. Metal-plated substrates whenever produced by the process claimed in any of the preceding claims.

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